



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 255/02, 290/04	A1	(11) International Publication Number: WO 98/42760 (43) International Publication Date: 1 October 1998 (01.10.98)
(21) International Application Number: PCT/US98/05552 (22) International Filing Date: 19 March 1998 (19.03.98) (30) Priority Data: 08/821,838 21 March 1997 (21.03.97) US (71) Applicant: EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520-5200 (US). (72) Inventor: SCHAUDER, Jean-Roch, Hector; 30, allée de Frenaie, B-1300 Wavre (BE). (74) Agents: SCHNEIDER, John, E. et al.; Exxon Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US).		(81) Designated States: AU, BR, CA, CN, JP, KR, MX, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: GRAFTED ETHYLENE COPOLYMERS		
(57) Abstract This invention relates to a grafted ethylene copolymer comprising ethylene and an alpha-olefin grafted with 0.1 weight % or more of an unsaturated acid or anhydride wherein the copolymer prior to grafting is characterized by: 1) a vinylidene to vinyl end chain unsaturation ratio of 3 or less, and 2) a CDBI of 60 % or more or was produced using one or more mono- or bis- cyclopentadienyl transition metal catalysts in combination with an activator of alumoxane and/or a non-coordinating anion, and the grafted copolymer is characterized by a number of unsaturated acid or anhydride molecules per chain of 2 or more as calculated according to the following formula: $[Mn^* \text{UAA}(\text{wt}\%)]/[\text{UAA}(\text{Mw})]$ wherein Mn is the number average molecular weight as measured by GPC, UAA(wt.%) is the weight percent of the unsaturated acid or anhydride as measured by FTIR spectroscopy and UAA(Mw) is the molecular weight of the unsaturated acid or anhydride.		

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Title: Grafted Ethylene Copolymers**Field of the Invention**

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This invention relates to grafted ethylene copolymers, compositions comprising the grafted ethylene copolymers, and a process to make the grafted ethylene copolymers.

Background of the Invention

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U.S. 5,346,963 describes substantially linear olefin polymers produced by Dow Chemical Company's "constrained geometry" catalysts grafted with an unsaturated organic compound which exhibit adhesive properties as well as imparting desirable impact properties to various thermoplastic polymer blends. These polymers however do not achieve high levels of grafting without an increase in viscosity.

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EPA 0 440 506 discloses derivatized ethylene alpha-olefin polymers useful as multifunctional viscosity index improvers. These polymers however are generally only functionalized at the chain end and have thus only one functionality per chain.

20

The chemistry used in this case generally leads to too low functionalization levels for the typical medium viscosity polymers used to modify engineering thermoplastics.

US 4 668 834 discloses epoxy grafted low molecular weight copolymers.

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Summary of the Invention

This invention relates to a grafted ethylene copolymer comprising ethylene and an alpha-olefin grafted with 0.1 weight% or more of an unsaturated acid or anhydride wherein the copolymer prior to grafting is characterized by:

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- 1) a vinylidene to vinyl end chain unsaturation ratio of 3 or less, and

2) a CDBI of 60 % or more if the polymer has a density of 0.90g/cc or more or a reactivity ratio between 0.5 and 1.5 or less if the polymer has a density of less than 0.90 g/cc,

and wherein the grafted copolymer is characterized by a number of unsaturated acid or anhydride molecules per chain of 2 or more as calculated according to the following formula: $[Mn * UAA (wt\%)] / [UAA(Mw)]$ wherein Mn is the number average molecular weight as measured by GPC, UAA(wt%) is the weight percent of the unsaturated acid or anhydride as measured by FTIR spectroscopy and UAA(Mw) is the molecular weight of the unsaturated acid or anhydride.

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Brief Description of the Figures

Figure 1 is a graph of the MFR increase during grafting for examples 1-8. (Cond.1 is example 1 and so on).

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Figure 2 is a graph of the MFR increase during grafting for examples 9-11. (Cond.9 is example 9 and so on).

Detailed Description

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This invention relates to a grafted ethylene copolymer comprising ethylene and an alpha-olefin grafted with 0.1 weight % or more of an unsaturated acid or anhydride wherein the copolymer prior to grafting:

1) has a vinylidene to vinyl end chain unsaturation ratio of 3 or less, and

25 2) was produced using a catalyst system comprising one or more mono- or bis-cyclopentadienyl transition metal catalysts in combination with an activator of alumoxane and/or a non-coordinating anion,

and

the grafted copolymer has a number of unsaturated acid or anhydride molecules per chain of 2 or more as calculated according to the following formula: $[Mn * UAA (wt\%)] / [UAA(Mw)]$ wherein Mn is the number average molecular weight as

30

measured by GPC, UAA(wt%) is the weight percent of the unsaturated acid or anhydride as measured by FTIR spectroscopy and UAA(Mw) is the molecular weight of the unsaturated acid or anhydride, and optionally

4) an Mw/Mn greater than $(I_{10}/I_2) - 4.63$.

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In a preferred embodiment the ethylene copolymer prior to grafting is a copolymer of ethylene and an α -olefin, preferably a C₃ to C₄₀ α -olefin, even more preferably a C₃ to C₁₈ α -olefin, even more preferably a C₃ to a C₁₂ α -olefin. In a preferred embodiment the ethylene polymer has a molecular weight distribution (Mw/Mn) of 4 or less, preferably 3 or less, even more preferably 2 or less, even more preferably between 2 and 1. In another preferred embodiment the ethylene copolymer has a Composition Distribution Breadth Index (CDBI) of 50 % or more, preferably 60% or more, even more preferably 70% or more, even more preferably 80% or more, even more preferably 90% or more. Composition Distribution Breadth Index (CDBI) is a measure of the composition distribution of monomer within the polymer chains and is measured by the procedure described in PCT publication WO 93/03093, published February 18, 1993 including that fractions having a weight average molecular weight (Mw) below 15,000 are ignored when determining CDBI.

20 The ethylene copolymer prior to grafting may have an Melt Index of 150 g/10min or less, preferably 20 g/10min or less, even more preferably 10 g/10min or less, even more preferably 5 g/10min or less.

25 In another preferred embodiment the ethylene copolymer prior to grafting has a number average molecular weight of 10,000 or more, more preferably 20,000 or more even more preferably 30,000 or more, even more preferably between 30,000 and 150,000.

30 In another preferred embodiment the ethylene copolymer prior to grafting has a ratio of methylenes to tertiary carbon atoms of 18 or less, more preferably 17 or less. In a

particularly preferred embodiment the ratio is 18 or less and the alpha-olefin is a C3 to C6 alpha-olefin, preferably butene, pentene, or hexene.

5 In another preferred embodiment the grafted ethylene copolymer has a number of unsaturated acid or anhydride molecules per chain of 2 or more as calculated according to the following formula: $[Mn * UAA (wt\%)] / [UAA(Mw)]$ wherein Mn is the number average molecular weight as measured by GPC, UAA(wt%) is the weight percent of the unsaturated acid or anhydride as measured by FTIR spectroscopy and UAA(Mw) is the molecular weight of the unsaturated acid or anhydride, preferably 3
10 or more, even more preferably 5 or more, even more preferably 10 or more.

The ethylene copolymer further comprises an unsaturated acid or anhydride. Preferred unsaturated acid or anhydride include any unsaturated organic compound containing at least one double bond and at least one carbonyl group. Representative
15 acids include carboxylic acids, anhydrides, esters and their salts, both metallic and non-metallic. Preferably the organic compound contains an ethylenic unsaturation conjugated with a carbonyl group ($-C=O$). Examples include maleic, fumaric, acrylic, methacrylic, itaconic, crotonic, α -methyl crotonic, and cinnamic acids as well as their anhydrides, ester and salt derivatives. Maleic acid and maleic anhydride, alone or in
20 combination, are particularly preferred. The unsaturated acid or anhydride is preferably present at about 0.1 weight % to about 20 weight %, preferably at about 0.2 weight % to about 10 weight %, even more preferably at about 0.3 to about 5 weight %, based upon the weight of the ethylene copolymer and the unsaturated acid or anhydride. This invention can also be practiced with any unsaturated monomer
25 which can be grafted in a reaction with peroxide.

Ethylene copolymers useful herein can be produced by the methods described in US 5,055,438; US 5,507,475; US 5,096,867; US 5,264,405; US 5,324,800; US 5,017,714; U.S. 5,240,894; US 5,198,401; US 5,153,157; WO 92 00333; WO 94
30 03506; EPA 520,732; EPA 129,368; EPA 277,003; EPA 277,004; and CA 1,268,753, which are incorporated by reference herein. Such polymers are available

from Exxon Chemical Company in Baytown, Texas under the Tradename EXACT™. In a preferred embodiment, the ethylene copolymers are produced using one or more mono- or bis-cyclopentadienyl transition metal (preferably group 4) catalysts in combination with an activator of alumoxane and/or a non-coordinating anion,

5 preferably in solution, slurry or gas phase. The catalyst may be supported or unsupported and the cyclopentadienyl rings by may substituted or unsubstituted. Several commercial products produced with such catalyst/activator combinations are commercially available from Exxon Chemical Company in Baytown Texas under the tradenames EXCEED™ and EXACT™. For more information on the methods and
10 catalysts/activators to produce such copolymers see WO 94/26816; WO 94/03506; EPA 277,003; EPA 277,004; US 5,153,157; US 5,198,401; US 5,240,894; US 5,017,714; CA 1,268,753; US 5,324,800; EPA 129,368; US 5,264,405; EPA 520,732; WO 92 00333; US 5,096,867; US 5,507,475; EPA 426 637; EPA 573 403; EPA 520 732; EPA 495 375; EPA 500 944; EPA 570 982; WO91/09882;
15 WO94/03506 and US 5,055,438. These polymers can be modified to contain the unsaturated acid or anhydride group by methods known in the art, such as U.S. Patents 3,326,917, 4,950,541 and 5,194,509, which are incorporated by reference herein.

20 Melt flow ratio measured as the ratio of I_{10} to I_2 (I_{10}/I_2) is measured by the procedure stated in ASTM D-1238.

Unsaturated acid or anhydride content is measured by FTIR (Fourrier Transformed Infrared Spectroscopy). The reaction products are compressed at temperature of
25 165°C into thin films from which infrared spectra were taken using a Mattson Polaris™ Fourier Transformed Infrared Spectrometer at 2 cm^{-1} resolution with the accumulation of 100 scans. The relative peak height of the anhydride absorption bond at 1790 cm^{-1} and of the acid absorption (coming from the anhydride hydrolysis in the air) at 1712 cm^{-1} compared with a bond at 4328 cm^{-1} serving as internal
30 standard is taken as a measurement of the MA content. %MA (total MA content) =

k (A1790 + A1712)/A4328, k being determined after internal calibration with a series of standards and having a value of 0.258 in this case.

The number of unsaturated acid or anhydride (UAA) molecules per polymer chain is obtained by multiplying the total unsaturated acid or anhydride content as measured by FTIR spectroscopy by the number average molecular weight divided by the unsaturated acid or anhydride molecular weight as described in equation:

$[M_n * \text{UAA (wt\%)}] / [\text{UAA (Mw)}]$ wherein M_n is the number average molecular weight as measured by GPC, UAA(wt%) is the weight percent of the unsaturated acid or anhydride as measured by FTIR spectroscopy and UAA(Mw) is the molecular weight of the unsaturated acid or anhydride

Unsaturation (vinylidene, vinyls chain end unsaturation, etc) in polyolefins are measured by proton NMR at 125°C. 100 mg of polymer is dissolved in 1cc of trichlorobenzene and 0.2 cc of deuterobenzene. The instrument is preferably a Variant™ Unity plus 300 MHz. The following parameters are preferably used: acquisition time: 3 sec, spectral window: 6000 Hz, pulse width: 30°, delay D1: 5 sec, number of transients: 1024, spinning rate: 17 Hz. For measurements described herein the following chemical shifts were assigned to the different proton types (and hence to the different unsaturation types): 5.6 - 5.9 ppm: $-\underline{\text{CH}}=\text{CH}_2$, 4.85 - 5.06: $-\text{CH}=\underline{\text{CH}}_2$, 5.3 - 5.55: $-\underline{\text{CH}}=\text{C}<$, 5.06 - 5.3 : $-\underline{\text{CH}}=\underline{\text{CH}}-$, 4.6 - 4.85: $>\text{C}=\underline{\text{CH}}_2$.

The same methods is used to measure methylenes and tertiary carbon atoms.

Reactivity ratio is measured by the ^{13}C NMR procedure described in K. Soga, Polymer Bulletin, 1983, Vol 10. pg 168.

Advantages of the grafted copolymers described herein include benefits derived from the lower viscosity ratios. Lower ratios translate into more stable operation conditions during processing of the polymers both during manufacturing and processing applications.

The grafted polymers of this invention can be used in blends with engineering thermoplastics possessing a functional group susceptible of chemically reacting or interacting through polar interactions or hydrogen bounding with the unsaturated monomer which has been grafted to the backbone. Typical thermoplastics
5 corresponding to this definition are polyamide-6, polyamide-6,6, polybutylene terephthalate, polyethylene terephthalate, polycarbonate, polyphenylene oxide, polyphenylene ether, polyoxymethylene, polyvinyl alcohol, ethylene acrylic acid copolymers, ethylene methylacrylate copolymers, ethylene acrylic acid methylacrylate terpolymers and polyvinyl chloride. These polymers can also be used in any of the
10 previous compositions also containing fillers such as silica, talc, calcium carbonate, carbon black or glass fibers.

Polymers of this invention can also be used as compatibilizers for blends of polyolefinic polymers and polar thermoplastics as the ones mentioned above. These
15 polymers can be added to polyolefinic compositions containing fillers such as talc, calcium carbonate, silica, carbon black and glass fibers where they will insure increased interaction with the filler and hence higher physical properties. Finally they can serve as adhesion promoters to polar substrates such as polar polymers, metal, aluminium, glass when used pure or in blends with other polyolefinic polymers but
20 also thermoset rubber compounds.

EXAMPLES

Mw and Mn are measured by gel permeation chromatography using monodisperse
25 polystyrene standards on a Waters 150 gel permeation chromatograph (GPC) coupled with a DRI detector and a Chromatix KMX-6 on line light scattering photometer. The system is used at 135 °C with 1,2,4-trichlorobenzene as the mobile phase. Shodex (from Showa Denks America, Inc.) polystyrene gel columns 802, 803, 804 and 805 were used. This technique is discussed on "Liquid Chromatography of
30 Polymers and Related Materials III" J. Cazes editor, Marcel Dekker, 1981, p207 which is incorporated by reference herein. No corrections for column spreading were

employed. Mw and Mn was calculated from elution times. The numerical analyses were performed using the commercially available Viscotek Co software in conjunction with the standard Gel Permeation package.

- 5 In the following examples the ungrafted copolymer and the grafted copolymer were tested for Melt Flow Ratio "MFR @ 230 °C"(g/10min) ASTM D 1238 (230 °C, 10 kg) and Melt Index (g/10min) ASTM 1238 D, condition E.

- EXACT™ 4049 is an ethylene-butene copolymer produced with a single site
10 metallocene catalyst which contains 26 wt% of butene and has a melt index (MI at 190°C, 2.16 kg) of 4.2 g/10 min and a density of 0.873 g/cm³.

EXACT™ 4033 is an ethylene butene copolymer containing 21.8 wt% butene and having a melt index (MI at 190°C, 2.16 kg) of 0.8 g/10 min and a density of 0.88 g/cm³.

- 15 ENGAGE™ 8100 is an ethylene octene copolymer containing 35.5 wt% of octene and having a melt index (MI at 190°C, 2.16 kg) of 1 g/10 min and a density of 0.87 g/cm³.

- ENGAGE™ 8200 is an ethylene octene copolymer containing 36.3 wt% of octene and having a melt index (MI at 190°C, 2.16 kg) of 4.7 g/10 min and a density of 0.87
20 g/cm³.

Examples 1-8:

- In a first set of eight experiments, EXACT 4033 and ENGAGE 8100 were melt
functionalized side by side on a non-intermeshing counter rotating twin screw
25 extruder (30 mm, L/D=48) as follows: 96 to 99 weight percent of polymer, 1 to 4 wt% of maleic anhydride, and 0.025 to 0.22 wt% of a 10% solution of Luperox™ 130 (Table 1) were fed to the extruder, at a polymer feed rate of 7kg/h, a screw speed of 250 rpm, over four temperatures zones respectively set at 180°C, 200°C, 210°C, 150°C with the die at 140°C. The polymer and the maleic anhydride
30 (Crystalman™) were simultaneously added to the feed hopper; after melting, the peroxide (Luperox™ 130) at a 10% concentration in mineral oil was added.

Unreacted maleic anhydride and decomposition products of the peroxide were removed with vacuum prior to polymer recovery. The individual experiment proportions of maleic anhydride and peroxide are reported in Table 1.

Table 1

Example	wt% maleic anhydride in feed	wt% Luperox 130 in the feed.
1	0.5	0.015
2	0.8	0.02
3	1	0.025
4	1	0.05
5	2	0.05
6	2	0.1
7	3	0.15
8	4	0.22

5

The data describing grafted polymers are reported in Table 2.

Table 2

Ex.	Exact 4033-g-MA (wt%MA)	MFR of Exact 4033-g-MA	MFR ratio	Engage 8100-g-MA (wt%MA)	MFR of Engage 8100-g-MA	MFR ratio
1	0.28	16.3	0.47	0.28	22	0.72
2	0.44	16.	0.48	0.45	24.7	0.64
3	0.8	15.6	0.49	0.73	19.3	0.82
4	0.7	13.	0.58	0.77	14.8	1.07
5	1.4	12.7	0.60	1.25	15.3	1.04
6	1.46	6.4	1.19	1.4	7.4	2.15
7	1.85	4.6	1.65	1.75	5.6	2.84
8	2.77	2.9	2.62	2.7	4.2	3.79

(MFR measured at 230 °C, 10kg, units g/10min) MFR ratio is the ratio of the MFR of the ungrafted copolymer to the MFR of the grafted copolymer. MA= maleic anhydride.

10

As can be seen from Table 2, although the grafting level is comparable, a higher viscosity ratio (illustrated by the ratio of the ungrafted polymer MFR to the grafted product MFR) is observed for the Engage polymer whatever the grafting conditions.

Examples 9-11:

In a second series of experiments, EXACT 4049 and ENGAGE 8200 were melt functionalized side by side on a non-intermeshing counter rotating twin screw extruder (30 mm, L/D=48) as follows: 97.8 to 98.5 weight percent of polymer, 1.5 to 2.2 wt% of maleic anhydride and 0.05 to 0.1 wt% of a 10% solution of LuperoxTM 130 (Table 3) were fed to the extruder, at a polymer feed rate of 7kg/h, a screw speed of 250 rpm, over four temperatures zones respectively set at 170°C, 190°C, 210°C, 210°C with the die at 180°C. The polymer and the maleic anhydride (CrystalmanTM) were simultaneously added to the feed hopper; after melting, the peroxide (Luperox 130) at a 10% concentration in mineral oil was added. Unreacted maleic anhydride and decomposition products of the peroxide are removed with vacuum prior to polymer recovery. The individual experiment proportions of maleic anhydride and peroxide are reported in Table 3. The characteristics of the grafted polymers are reported in Table 4.

Table 3

Example	wt% maleic anhydride in feed	wt% Luperox 130 in the feed.
9	1.5	0.05
10	1.9	0.075
11	2.2	0.1

Table 4

Ex	Exact 4049-g-MA (wt% MA)	MFR of Exact 4049-g-MA	MFR ratio	Engage 8200-g-MA (wt%MA)	MFR Engage 8200-g-MA	MFR Ratio
9	1.27	0.9	4.7	1.27	0.9	5.2
10	1.63	0.7	6.0	1.58	0.6	7.8
11	1.78	0.5	8.4	1.71	0.3	15.7

(MFR measured at 190 °C and 2.16kg, units are g/10min); MA= maleic anhydride

As seen before, the MFR increase is higher with the Engage polymer. In this case, the viscosity increase is higher compared to the increase observed in examples 1-8. Without wishing to be bound by theory, this has been attributed to the lower initial

viscosity and hence lower molecular weight of the raw polymer which has a higher end chain number and hence a higher unsaturation level (Table 5).

Maleic anhydride (MA) content was measured by FTIR (Fourrier Transformed
5 Infrared Spectroscopy). The reaction products are compressed at temperature of 165°C into thin films from which infrared spectra were taken using a Mattson Polaris™ Fourier Transformed Infrared Spectrometer at 2 cm⁻¹ resolution with the accumulation of 100 scans. The relative peak height of the anhydride absorption bond at 1790 cm⁻¹ and of the acid absorption (coming from the anhydride hydrolysis
10 in the air) at 1712 cm⁻¹ compared with a bond at 4328 cm⁻¹ serving as internal standard is taken as a measurement of the MA content.

%MA (total MA content) = k (A1790 + A1712)/A4328, k being determined after internal calibration with a series of standards and having a value of 0.258 in this case.

15 The number of unsaturated acid or anhydride molecules per polymer chain, for example the number of maleic anhydride(MA) molecules per chain, is obtained by multiplying the total MA content as measured by FTIR spectroscopy by the number average molecular weight divided by the MA molecular weight as described in equation:

20
$$[M_n \cdot \text{MA (wt\%)}] / [\text{MA (Mw)}]$$

wherein the M_n is the number average molecular weight as measured by GPC, MA(wt%) is the weight percent of the maleic anhydride as measured by FTIR spectroscopy and MA(Mw) is the molecular weight of the maleic anhydride.

25 Unsaturations (vinylidene, vinyl chain end unsaturation, etc) in polyolefins were measured by proton NMR at 125°C. The 100 mg of polymer were dissolved in 1cc of trichlorobenzene and 0.2 cc of deuterobenzene. The instrument was a Variant™ Unity plus 300 MHz. The following parameters were used: aquisition time: 3 sec, spectral window: 6000 Hz, pulse width: 30°, delay D1: 5 sec, number of transients:
30 1024, spinning rate: 17 Hz. The following chemical shifts have been assigned to the different proton types (and hence to the different unsaturation types): 5.6 - 5.9 ppm:-

$\text{CH}=\text{CH}_2$, 4.85 - 5.06. $-\text{CH}=\text{CH}_2$, 5.3 - 5.55. $-\text{CH}=\text{C}<$, 5.00 - 5.5. $-\text{CH}=\text{CH}$, 4.0 - 4.85. $>\text{C}=\text{CH}_2$.

Table 5 reports the characterization for the four ungrafted polymers.

Table 5

	EX. 4049	EX. 4033	ENG. 8100	ENG. 8200
$-\text{CH}=\text{CH}_2$ per 1000 C	0.06	0.04	0.01	0.02
$-\text{CH}=\text{CH}-$ per 1000 C	0.08	0.05	0.08	0.12
$-\text{CH}=\text{C}<$ per 1000 C	0.15	0.08	0.04	0.09
$>\text{C}=\text{CH}_2$ per 1000 C	0.09	0.05	0.07	0.1
TOTAL unsatur. per 1000 C	0.38	0.22	0.2	0.33
$>\text{C}=\text{CH}_2/-\text{CH}=\text{CH}_2$ (vinylidene/vinyl ratio)	1.5	1.3	7.0	5.0
$-\text{CH}=\text{CH}_2$ per Mn	0.17	0.18	0.04	0.06
$-\text{CH}=\text{CH}-$ per Mn	0.22	0.23	0.33	0.35
$-\text{CH}=\text{C}<$ per Mn	0.42	0.37	0.16	0.26
$>\text{C}=\text{CH}_2$ per Mn	0.25	0.23	0.29	0.29
TOTAL unsatur. per Mn	1.06	1.01	0.81	0.97
COMPOSITION	EX. 4049	EX. 4033	ENG. 8100	ENG. 8200
Density	0.873	0.88	0.87	0.87
wt% C_2	74.0	78.2	64.5	63.7
wt% C_4	26.0	21.8	0.0	0.0
wt% C_8	0.0	0.0	35.5	36.3
wt% C_3	0.0	0.0	0.0	0.0
$-\text{CH}_2$ per 1000 C	869	890	911	909
$-\text{CH}$ per 1000C	65	54	44	45
$-\text{CH}_2/-\text{CH}$ ratio	13.4	16.5	20.7	20.2
GPC-DRI				
$\text{Mn} \cdot 10^{-3}$	39	64	57	41
$\text{Mw} \cdot 10^{-3}$	74	121	103	77
Mw/Mn	1.9	1.9	1.8	1.9

In a preferred embodiment the grafted copolymers of this invention achieve a similar level of grafting with less increase in viscosity versus known polymers. Note that in Figure 1 the copolymers of the invention had a much lower MFR ratio.

Claims:

1. A grafted ethylene copolymer comprising ethylene and an alpha-olefin grafted with 0.1 weight% or more of an unsaturated acid or anhydride wherein the copolymer prior to grafting is characterized by:
- 5 1) a vinylidene to vinyl end chain unsaturation ratio of 3 or less, and
2) a CDBI of 60 % or more, and
wherein the grafted copolymer is characterized by a number of unsaturated acid or anhydride molecules per chain of 2 or more as calculated according to the following
- 10 formula: $[Mn * UAA (wt\%)] / [UAA(Mw)]$ wherein Mn is the number average molecular weight as measured by GPC, UAA(wt%) is the weight percent of the unsaturated acid or anhydride as measured by FTIR spectroscopy and UAA(Mw) is the molecular weight of the unsaturated acid or anhydride.
- 15 2. The copolymer of claim 1 wherein CDBI is 80% or more.
3. The copolymer of claim 1 wherein the copolymer prior to grafting has an Mw/Mn greater than $(I_{10}/I_2) - 4.63$.
- 20 4. The copolymer of claim 1 wherein the alpha-olefin is a C₃ to a C₁₂ alpha-olefin.
5. The copolymer of claim 1 wherein the copolymer prior to grafting has a melt index of 10 g/10min or less.
- 25 6. The copolymer of any of claim 1 where the copolymer prior to grafting has a number average molecular weight between 30,000 and 150,000.
7. The copolymer of claim 1 wherein the copolymer prior to grafting has a ratio of methylenes to tertiary carbon atoms of 18 or less and the alpha-olefin is butene, pentene or hexene.
- 30 8. The copolymer of claim 1 wherein the grafted copolymer has a number of unsaturated acid or anhydride molecules per chain of 5 or more.
- 35 9. The copolymer of claim 1 wherein the unsaturated acid or anhydride is maleic acid, maleic anhydride or a combination thereof.

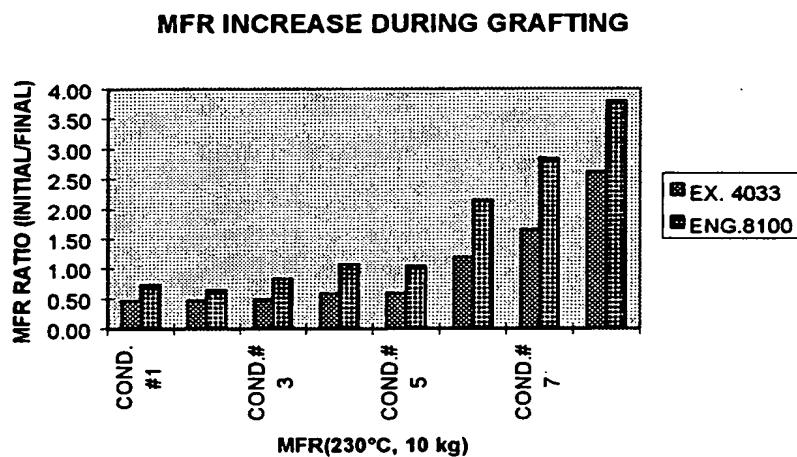
10. The copolymer of any of the above claims wherein the copolymer prior to grafting was produced using one or more mono- or bis-cyclopentadienyl transition metal catalysts in combination with an activator of alumoxane and/or a non-coordinating anion.

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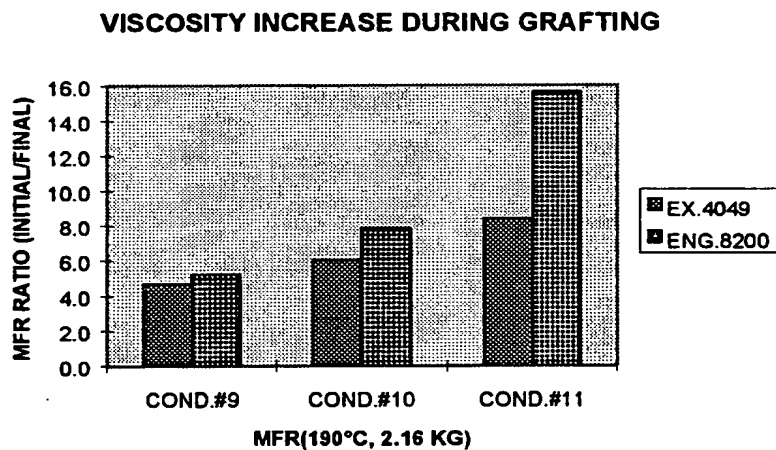
11. The copolymer of claim 10 wherein mono- or bis-cyclopentadienyl transition metal catalysts is a biscyclopentadienyl group 4 compound.

Figure 1

1/1



5 Figure 2



INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/05552

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F255/02 C08F290/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 28486 A (GUENTHER WOLFGANG ; OPPENLAENDER KNUT (DE); BASF AG (DE); FAUL DIET) 19 September 1996 see page 3, line 28-40 ---	
A	US 5 310 806 A (WILD LESLIE ET AL) 10 May 1994 see column 3, line 46-68 -----	1



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

Special categories of cited documents:

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Date of the actual completion of the international search

30 June 1998

Date of mailing of the international search report

09/07/1998

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/05552

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		AU 5100896 A	02-10-1996
		CA 2213009 A	19-09-1996
		EP 0815150 A	07-01-1998
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US 5310806 A	10-05-1994	NONE	
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